Comparison of Particulate Nitrate Formation in Different Chemical Regimes

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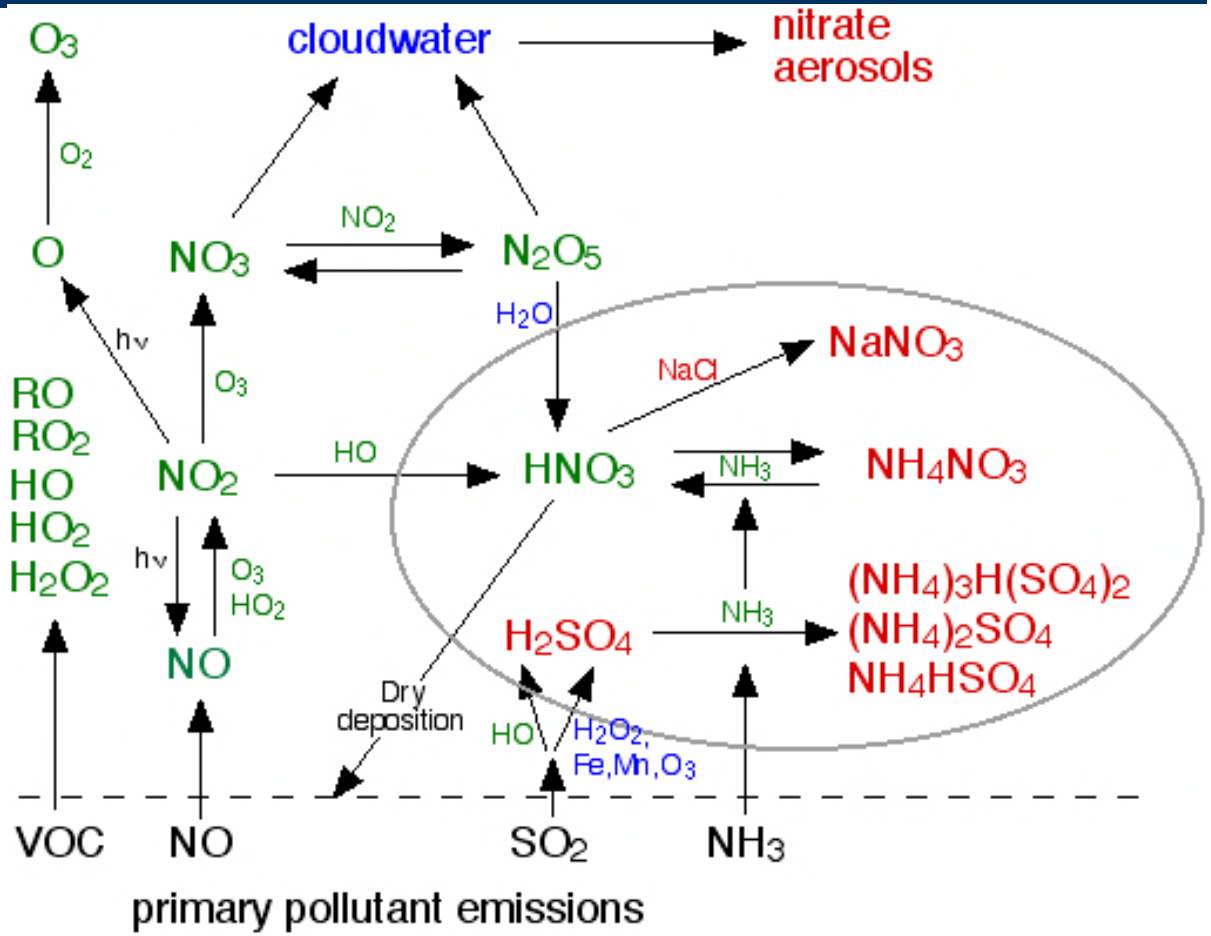
Overview – *Applications of Equilibrium Models*

- **Locations**
  - Central and southern California (SCAQS, CADMP, IMS95)
  - Midwest (MMW)
  - Southeastern US (SEARCH)
- **Approach**
  - Apply SCAPE2 and ISORROPIA
  - Compare predictions and measurements
  - Run scenarios with reduced sulfate, HNO_3, or NH_3

Scope of Modeling –
Partition Between Gas and Condensed Phases



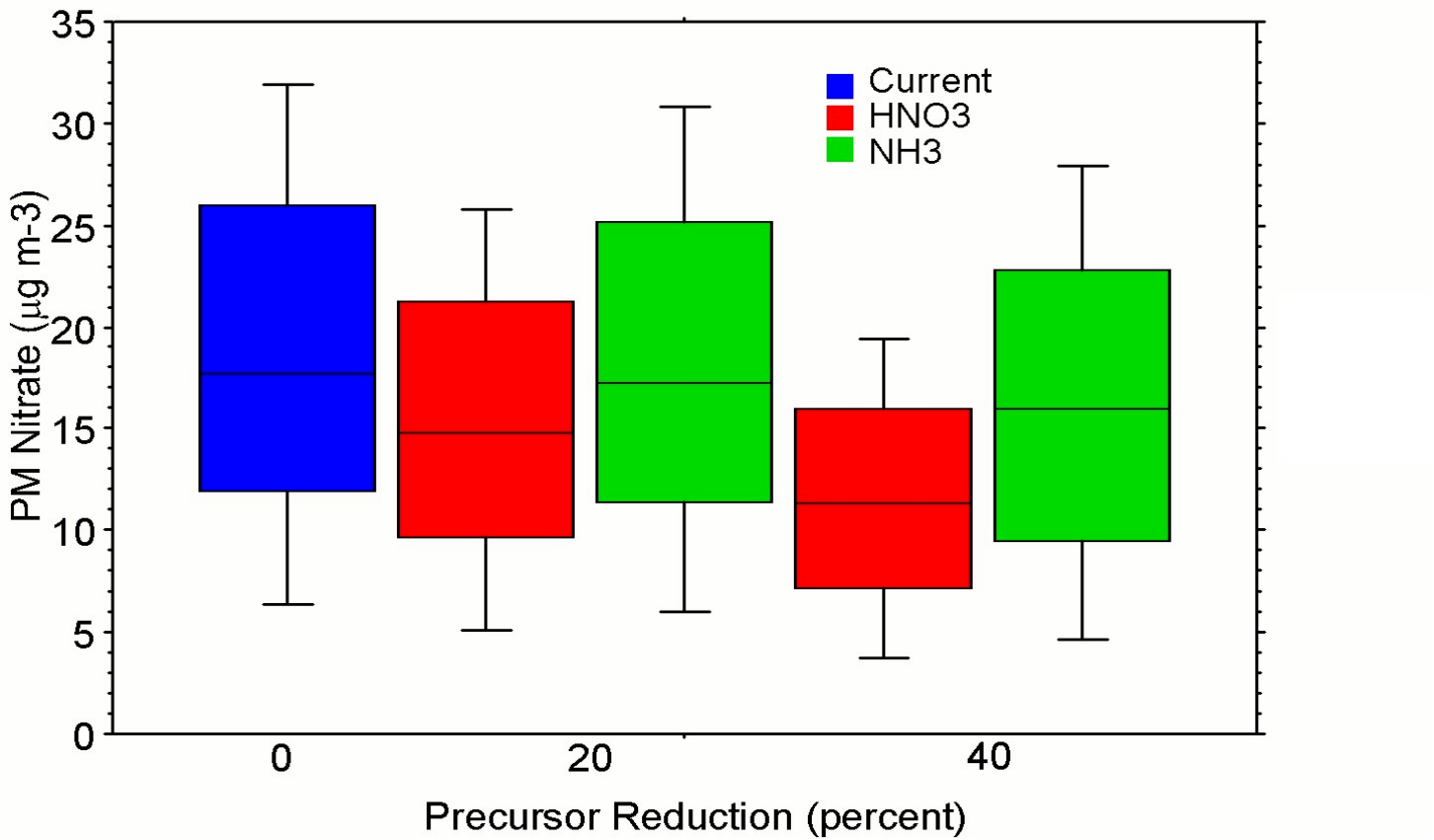
Accuracy of Model Predictions – *Select Days and Check Predictions*

- Exclude high-RH (>95 %) days
- Simulate each sample
- Compare predictions with measurements

How Does PM Nitrate Respond – *Evaluate Reduced Sulfate, HNO_3, or NH_3*

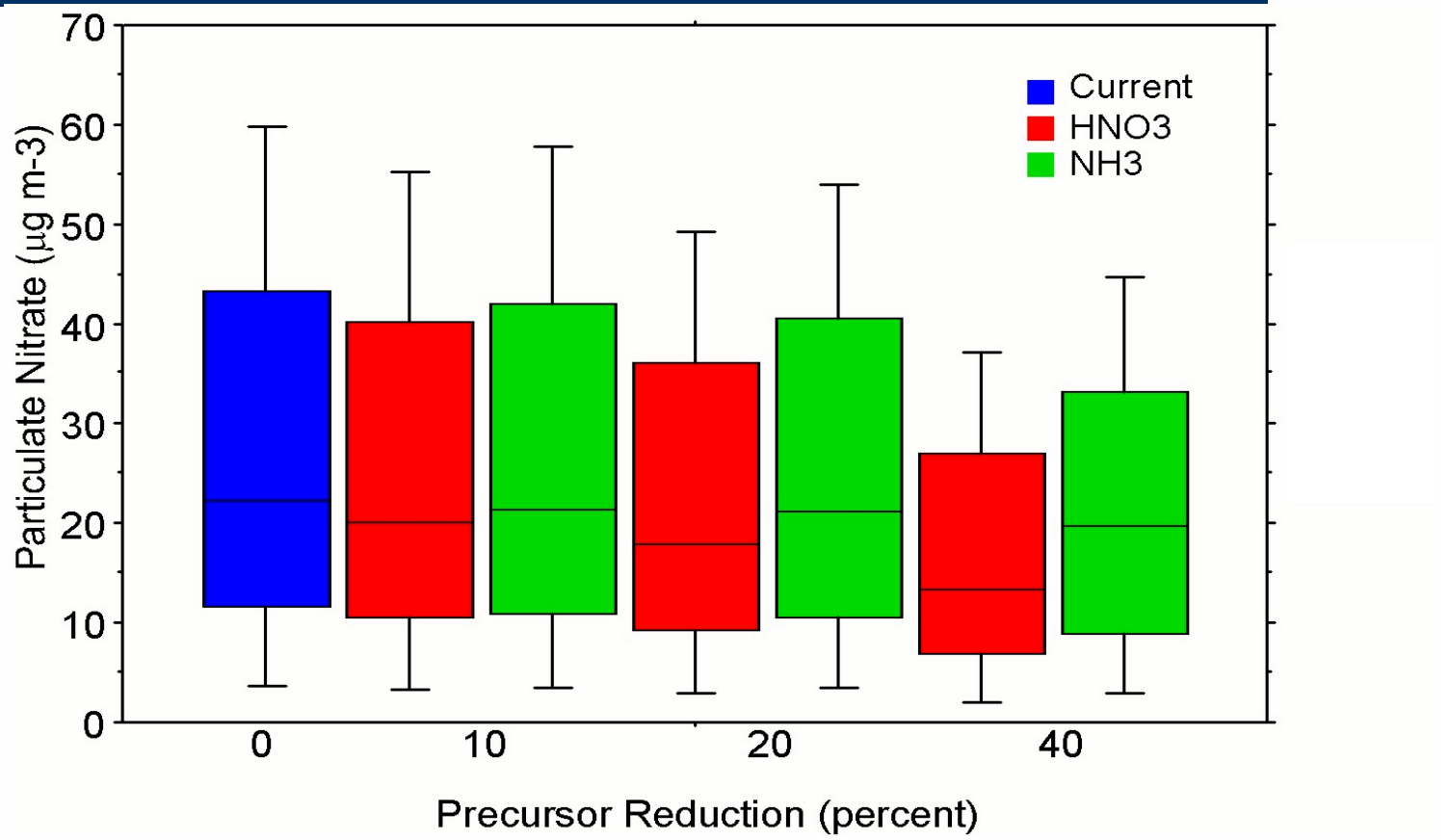
- ~20 to 300 individual samples per site
- 3 hour – 24 hour sample duration
- 10 to 30 simulations for each sample
- Reduce sulfate, or HNO_3, or NH_3 in increments of 10 to 20 percent
- Examine changes in PM nitrate
- Summarize using sample means and distributions

California, San Joaquin Valley – *PM NO_3 Decreases as HNO_3 Decreases*



IMS95 winter 1995-96 – 4 sites

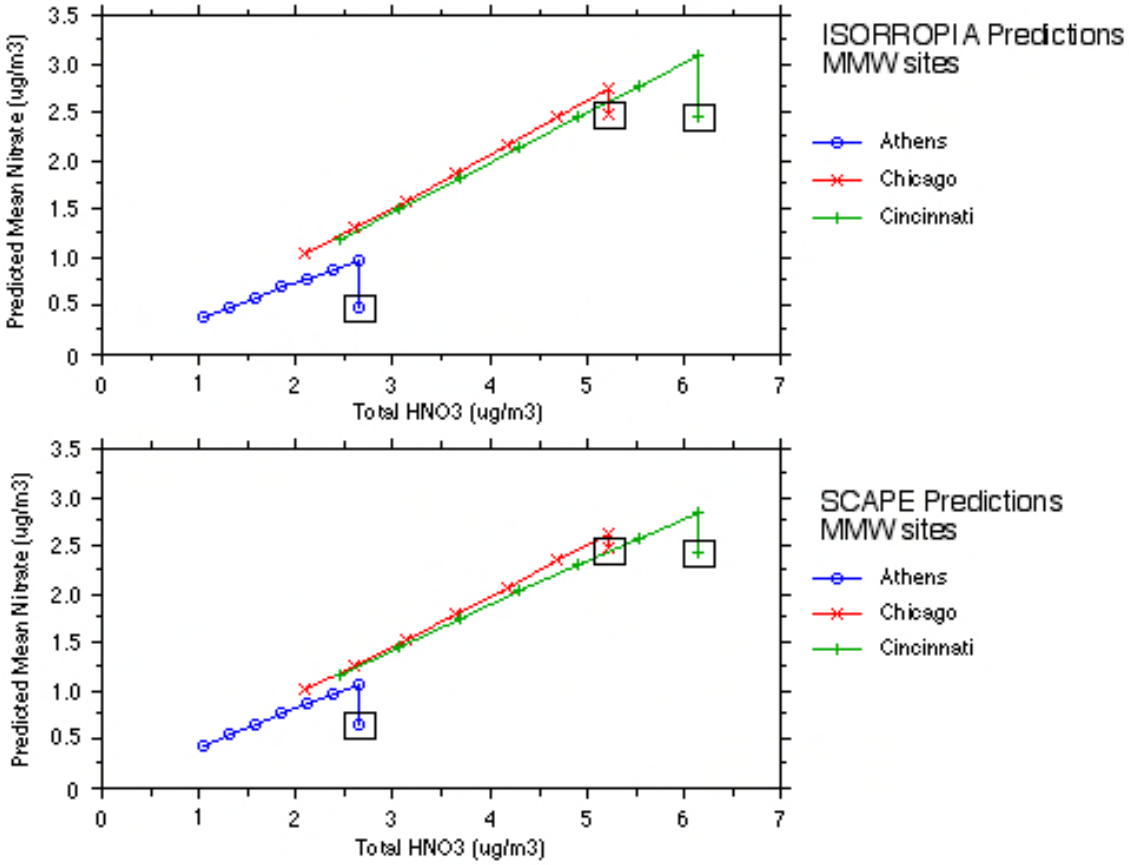
Southern California –
PM NO_3 Decreases as HNO_3 Decreases



SCAQS winter 1987 – 5 sites

Midwest – When SO_4 Decreases – *NO_3 Up, Then Declines as HNO_3 Decreases*

Current conditions (in boxes) compared to 50% lower sulfate with varied HNO_3

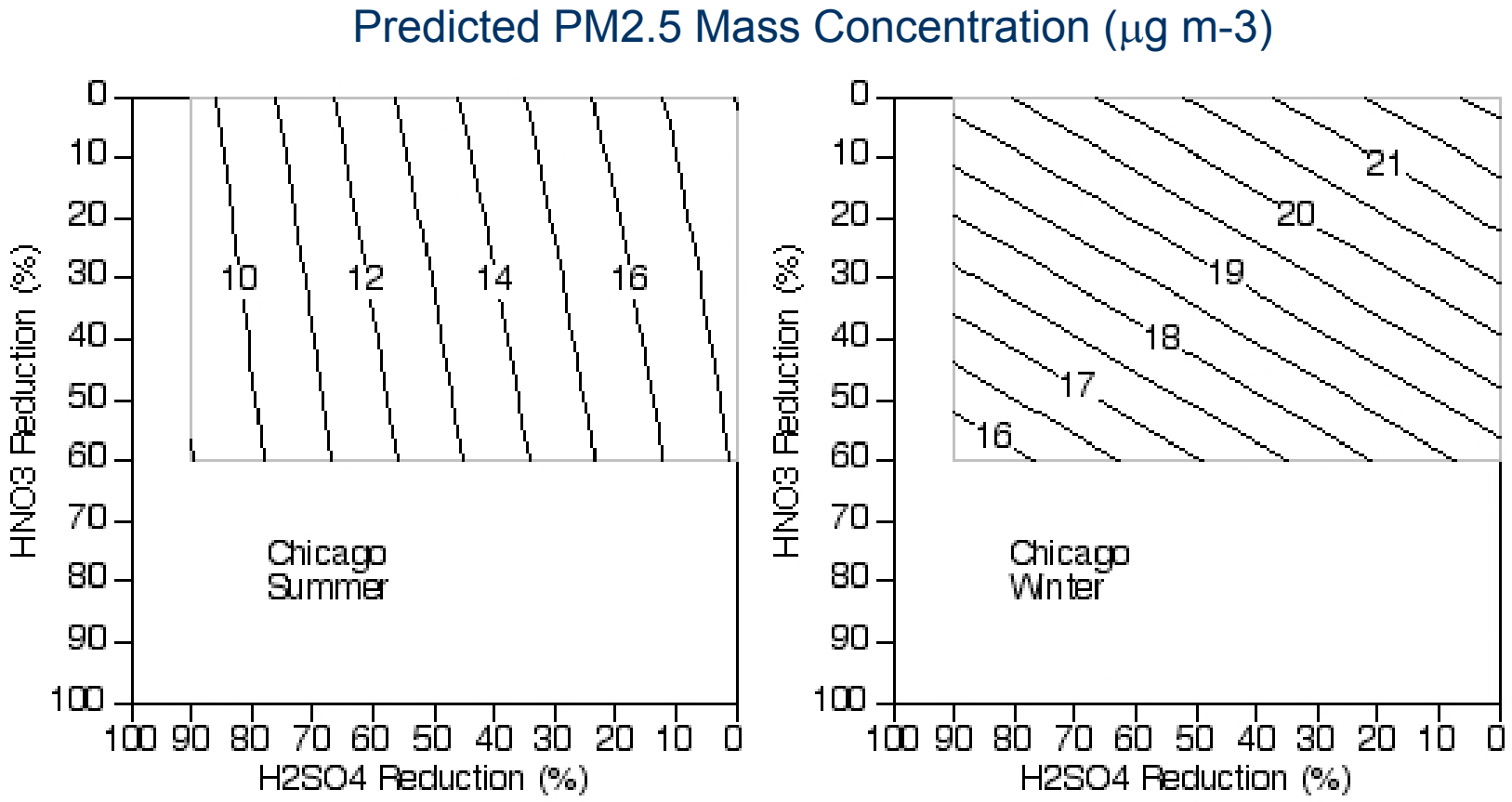


Aug-Sep 1999
Jan-Feb 2000

Isopleths of Predicted Fine PM – *Compact Graphical Representation*

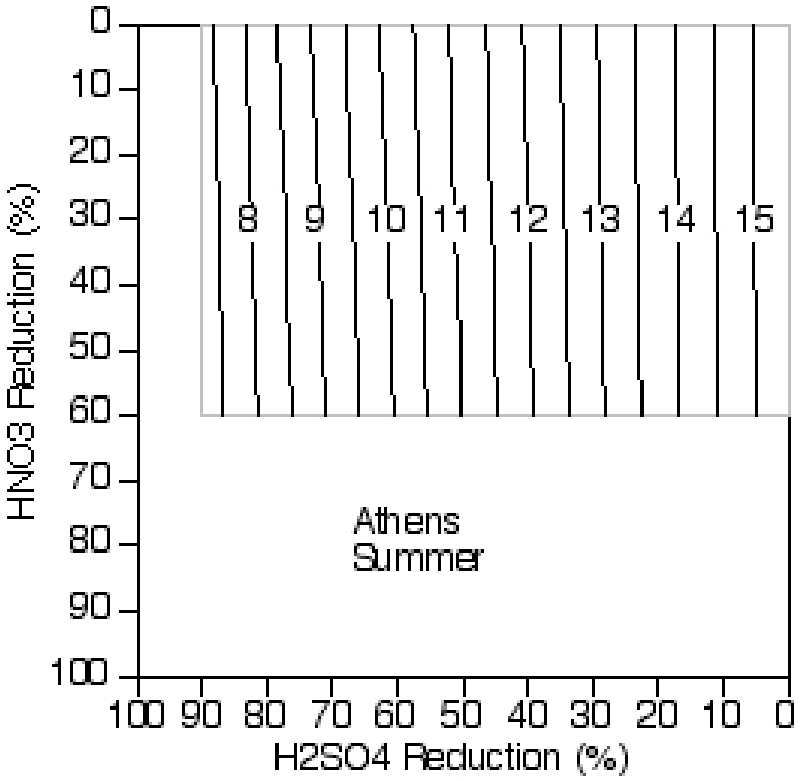
- What are net effects of changes in sulfate, HNO_3, and NH_3?
- Predict PM mass change
  - measured fine mass minus change in inorganics
  - inorganics = sum of sulfate, nitrate, ammonium
- Means of individual samples

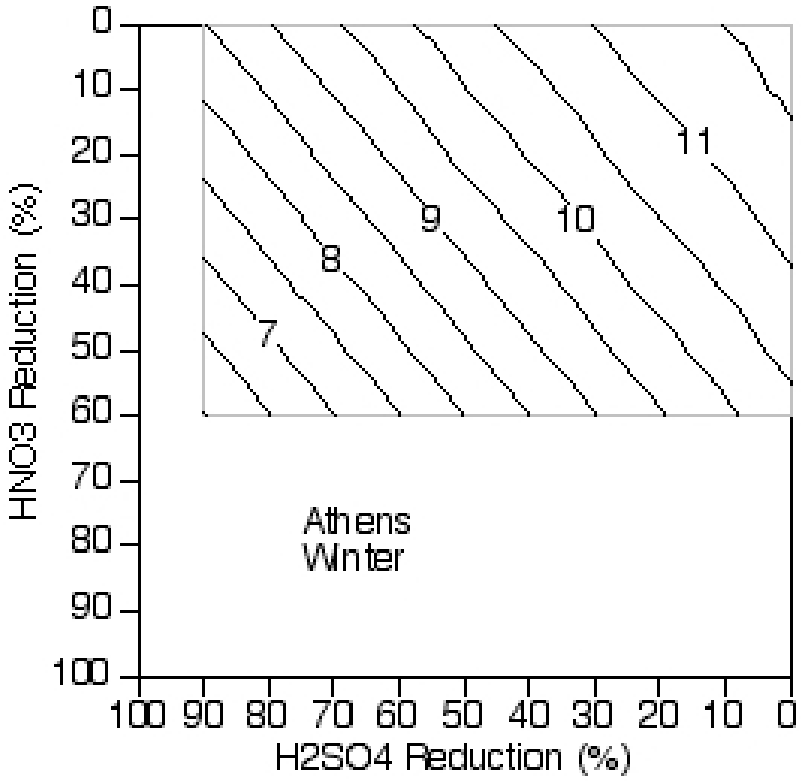
MARCH Midwest Urban Sites – *Seasonal Sensitivity to HNO_3*



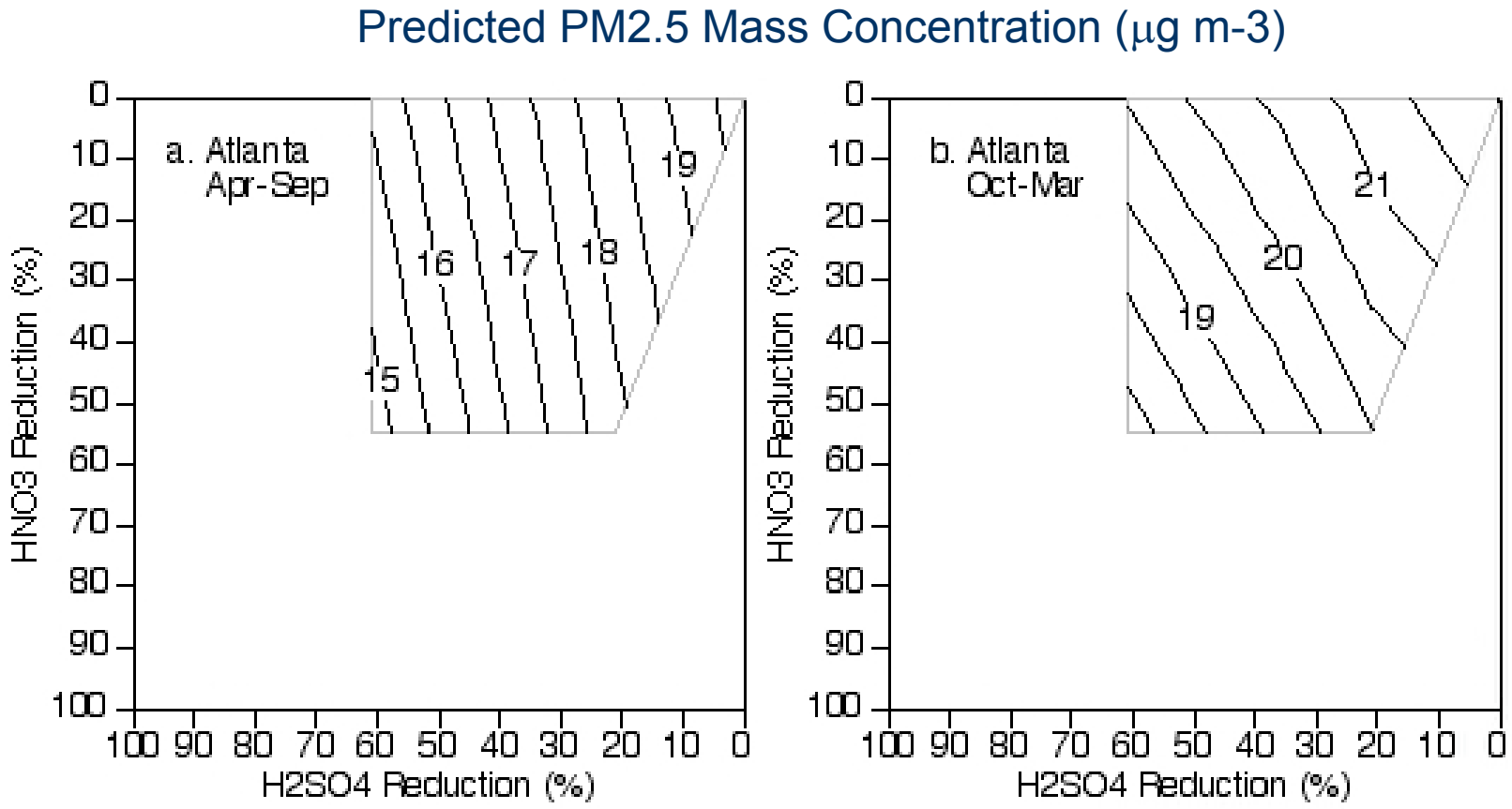
MARCH Midwest Rural Site – *Winter Sensitivity to HNO_3*

Predicted PM2.5 Mass Concentration (μg m-3)





SEARCH Atlanta Site – *Limited Sensitivity to HNO_3*



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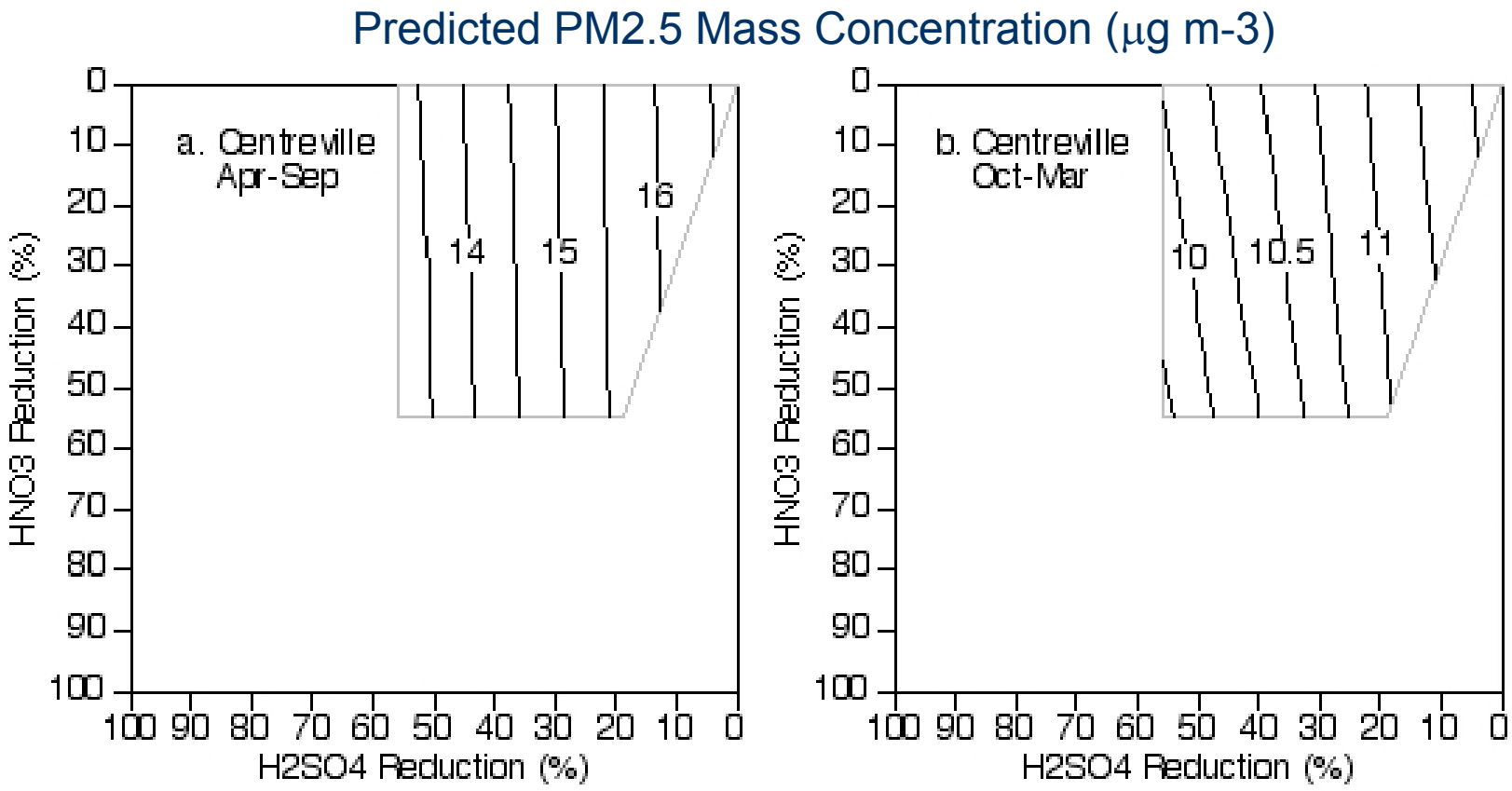
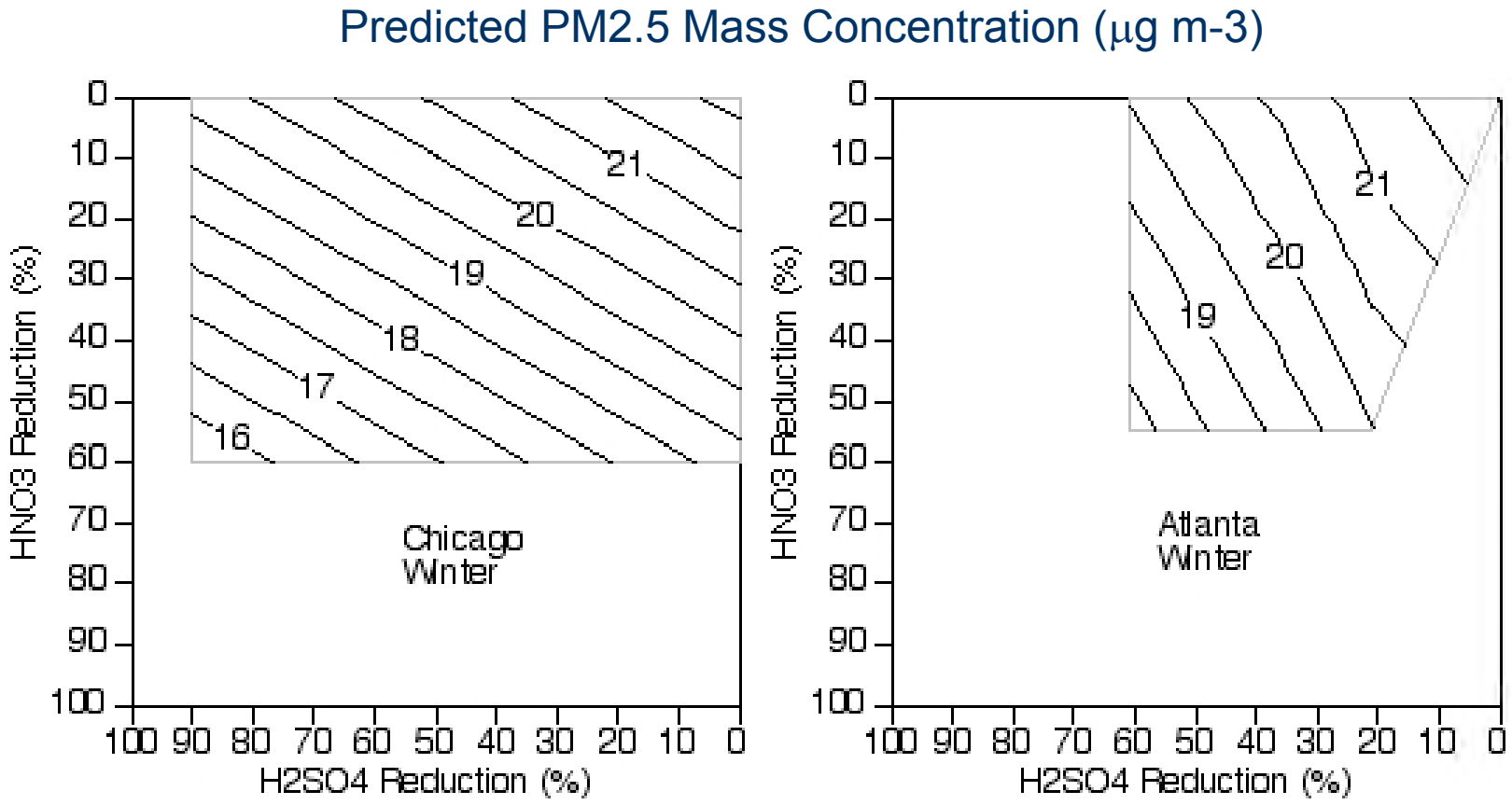
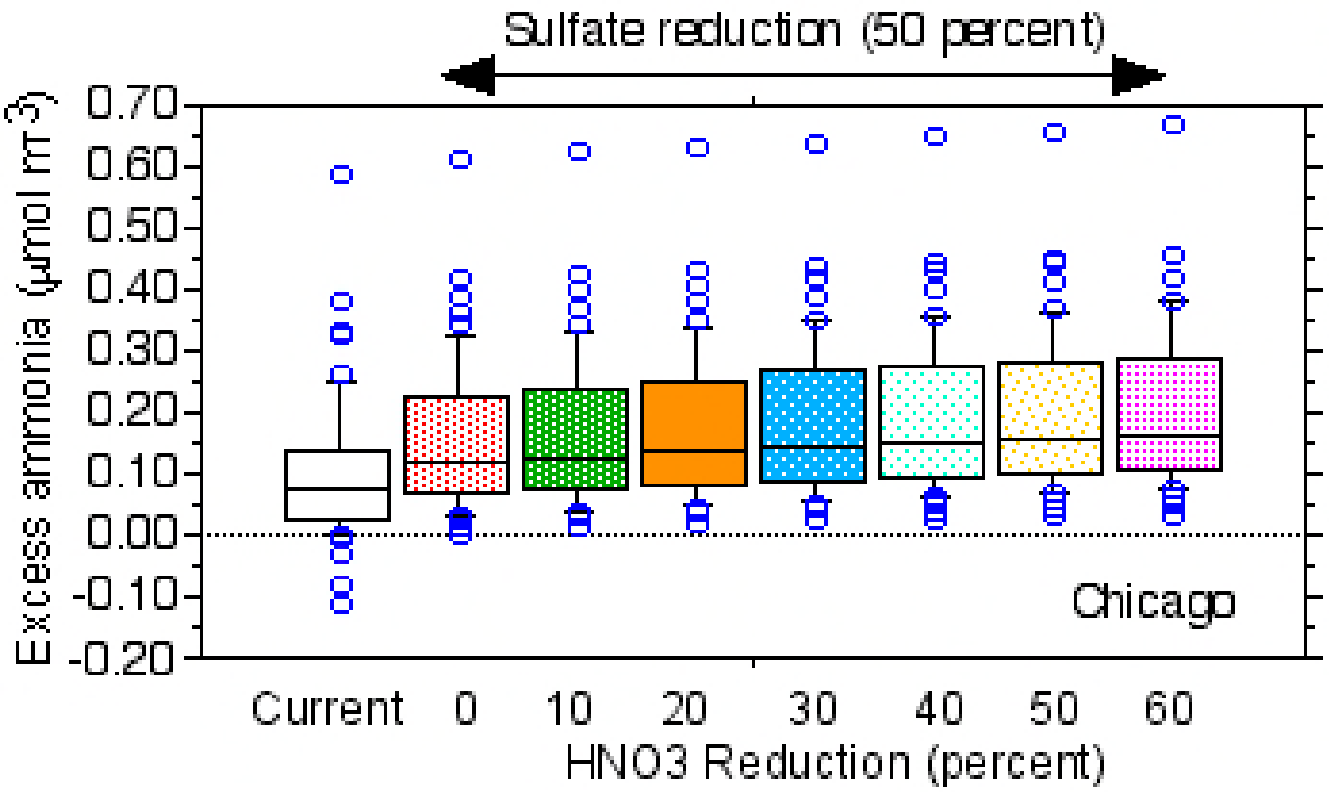


Atlanta Compared With Chicago – *Atlanta Less Sensitive to HNO_3*

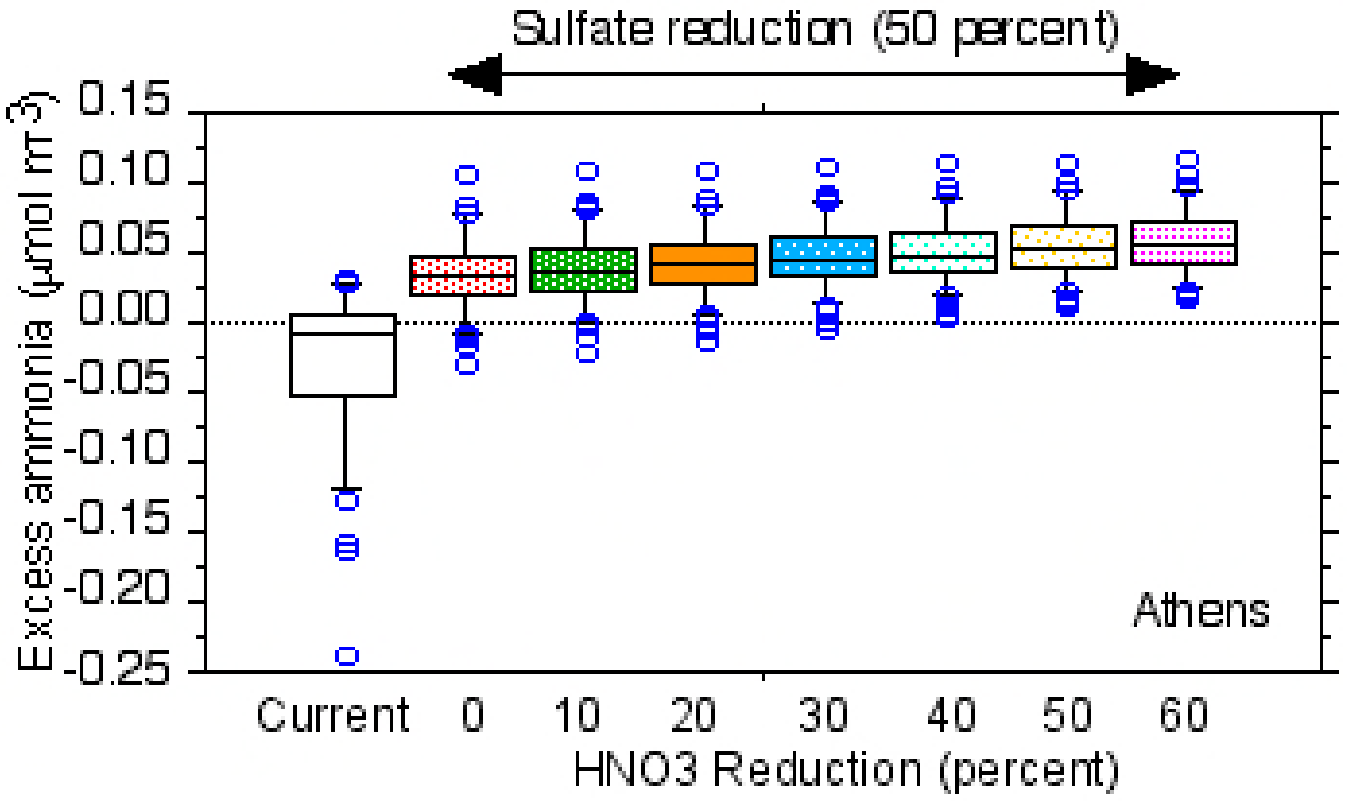


Sulfate Reduction in Chicago - *Many Samples Currently NH_3-Rich*



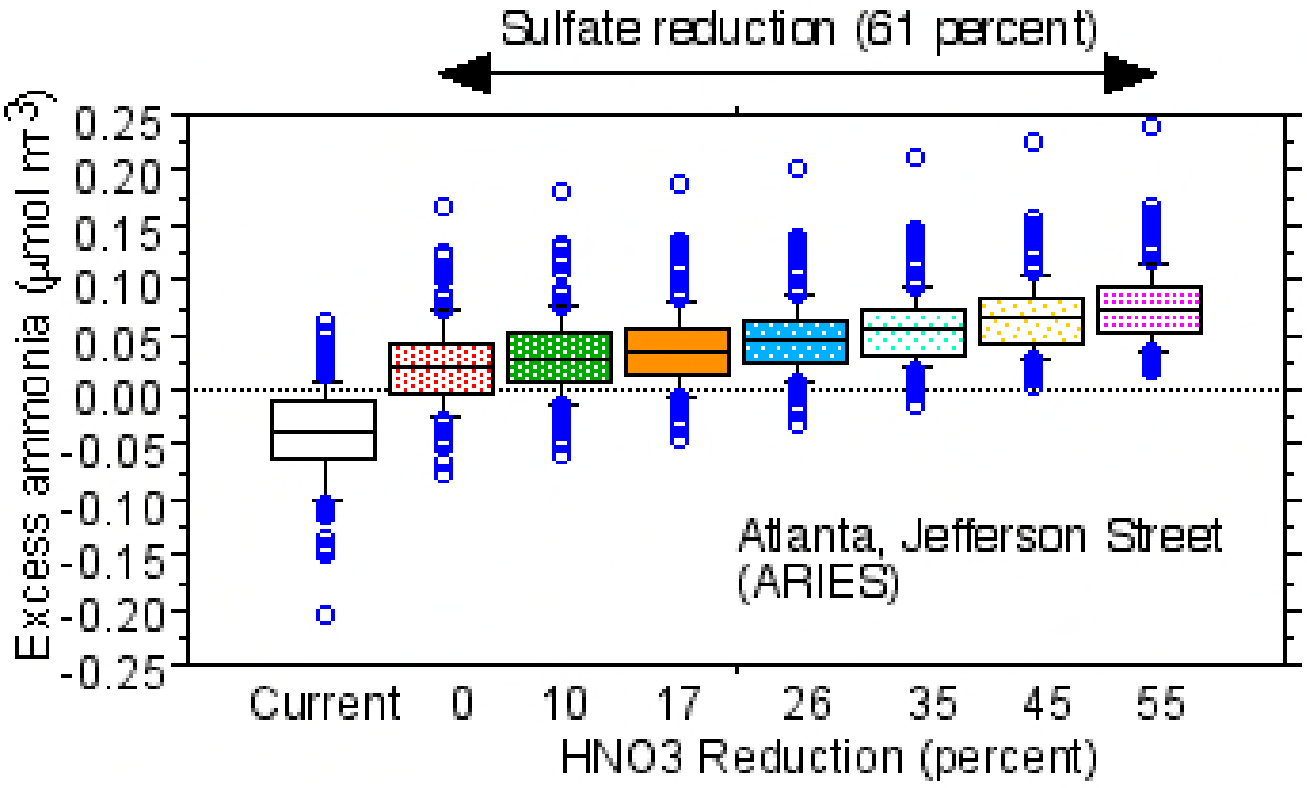
Current conditions compared to 50% lower sulfate and 10-60% lower HNO_3

Sulfate Reduction in Rural MW - *Shifts From NH_3-Poor to NH_3-Rich*



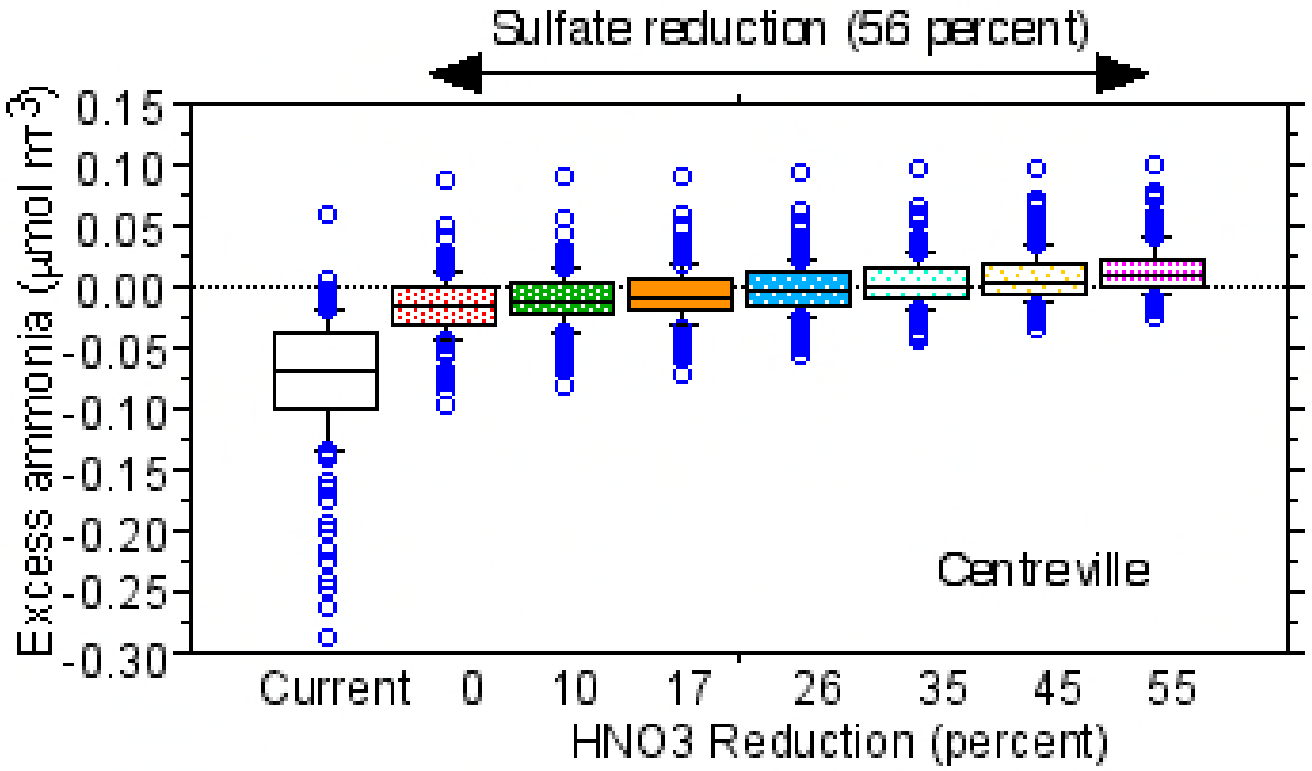
Current conditions compared to 50% lower sulfate and 10-60% lower HNO_3

Sulfate Reduction in Atlanta - *Shifts From NH_3-Poor to NH_3-Rich*



Current conditions compared to 61% lower sulfate and 10-55% lower HNO_3

Sulfate Reduction in Rural SE - *Composition Remains NH_3-Limited*



Current conditions compared to 56% lower sulfate and 10-55% lower HNO_3

Conclusions

- PM nitrate formation is more ammonia-limited in the SE US than in Midwest and California – ammonia sources?
- Mean PM mass concentrations always decrease in response to sulfate reductions but by different amounts due to varying responses of PM nitrate
- PM nitrate response depends upon availability of ammonia – control strategy?